

## WHAT IS CLAIMED IS:

1. An article comprising a substrate, the substrate having electrolytically deposited thereon a coating, said coating comprising a mixture of a calcium phosphate compound and chitosan.
2. An article as set forth in claim 1 wherein the calcium phosphate compound is selected from the group consisting of monetite, brushite, amorphous calcium phosphate and whitlockite.
3. An article as set forth in claim 1 wherein the substrate is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, tin, cobalt, aluminum, chromium, molybdenum, tungsten, titanium vanadium aluminum alloys, cobalt chromium molybdenum alloys, and combinations thereof.
4. An article as set forth in claim 3 wherein the substrate further comprises a second coating selected from the group consisting of carbon and nitride.
5. An article as set forth in claim 4 wherein the second coating is from about 100 nanometers to about 100 micrometers thick.
6. An article as set forth in claim 1 wherein the coating has a thickness of at least about 5 micrometers.
7. An article as set forth in claim 6 wherein the coating has a thickness of at least about 10 micrometers.
8. An article as set forth in claim 6 wherein the coating has a thickness of at least about 25 micrometers.
9. An article as set forth in claim 1 wherein the coating comprises at least about 1% chitosan.

10. An article as set forth in claim 9 wherein the coating comprises at least about 10% chitosan.

11. An article comprising a substrate, the substrate having electrolytically deposited thereon a coating, said coating comprising a mixture of hydroxyapatite and chitosan.

12. An article as set forth in claim 11 wherein the substrate is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, tin, cobalt, aluminum, chromium, molybdenum, tungsten, titanium vanadium aluminum alloys, cobalt chromium molybdenum alloys, and combinations thereof.

13. An article as set forth in claim 12 wherein the substrate further comprises a second coating selected from the group consisting of carbon and nitride.

14. An article as set forth in claim 13 wherein the second coating is from about 100 nanometers to about 100 micrometers thick.

15. An article as set forth in claim 11 wherein the coating has a thickness of at least about 5 micrometers.

16. An article as set forth in claim 15 wherein the coating has a thickness of at least about 10 micrometers.

17. An article as set forth in claim 15 wherein the coating has a thickness of at least about 25 micrometers.

18. An article as set forth in claim 11 wherein the coating comprises at least about 1% chitosan.

19. An article as set forth in claim 18 wherein the coating comprises at least about 10% chitosan.

TOGETHER

20. A method of electrolytically depositing two species simultaneously as a composite coating on an article, the article comprising a substrate, the composite coating comprising a mixture of a calcium phosphate containing compound and chitosan, the method comprising:

5           introducing a cathode and an anode into an electrolytic apparatus, the cathode comprising a substrate to be coated with a composite electrolytic coating comprised of two species;

                  introducing an electrolyte solution in the electrolytic apparatus such that the electrolyte solution contacts the cathode and the anode, the electrolyte solution  
10           comprising calcium ions, phosphate ions, and chitosan ions;

                  passing a current between the anode and the cathode to promote the growth of the composite coating on the cathode, the composite coating comprising a mixture of the calcium phosphate containing compound and chitosan.

21. The method as set forth in claim 20 wherein the cathode is comprised of a conductive material selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, tin, cobalt, aluminum, chromium, molybdenum, tungsten, titanium vanadium aluminum alloys, cobalt chromium molybdenum alloys, and  
5           combinations thereof.

22. The method as set forth in claim 20 wherein the calcium phosphate containing compound is deposited on the cathode in the form of brushite.

23. The method as set forth in claim 20 wherein the calcium phosphate containing compound is deposited on the cathode in the form of monetite.

24. The method as set forth in claim 20 wherein the calcium phosphate containing compound is deposited on the cathode in the form of amorphous calcium phosphate.

25. The method as set forth in claim 20 wherein the current passed between the anode and the cathode is from about 1mA/cm<sup>2</sup> to about 1 Amp/cm<sup>2</sup>.

26. The method as set forth in claim 25 wherein the current passed between the anode and the cathode is about 100 mA/cm<sup>2</sup>.

27. The method as set forth in claim 20 wherein the electrolyte solution has a pH of from about 1.5 to about 7.

28. The method as set forth in claim 20 wherein the electrolyte solution has a pH of from about 1.5 to about 5.

29. The method as set forth in claim 20 wherein the electrolyte solution has a pH of from about 2 to about 4.

30. The method as set forth in claim 20 wherein the concentration of chitosan in the electrolyte solution is from about 0.02% to about 5%.

31. The method as set forth in claim 20 wherein the concentration of chitosan in the electrolyte solution is from about 0.1% to about 1%.

32. The method as set forth in claim 20 wherein the resulting composite coating has a thickness of at least about 5 micrometers.

33. The method as set forth in claim 20 wherein the resulting composite coating has a thickness of at least about 25 micrometers.

34. The method as set forth in claim 20 wherein the temperature of the electrolyte solution is from about 10°C to about 70°C.

35. The method as set forth in claim 20 further comprising the step of treating the resulting composite coating with a base solution to produce a composite coating comprised of chitosan and hydroxyapatite.

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36. The method as set forth in claim 35 wherein the base solution is selected from the group consisting of sodium hydroxide, potassium hydroxide and sodium phosphate.

37. A method of electrolytically coating an article with a composite layer, the article comprising a substrate, the composite layer comprising a mixture of a calcium phosphate containing compound and chitosan, the method comprising:

- 5 introducing a cathode and an anode into an electrolytic apparatus, the cathode comprising a substrate to be coated with the composite layer;
- introducing a first electrolyte solution in the electrolytic apparatus such that the electrolyte solution contacts the anode and the cathode, the first electrolyte solution comprising calcium and phosphate ions;
- 10 passing a current between the anode and the cathode to promote the growth of a calcium phosphate containing compound on the cathode;
- introducing a second electrolyte solution into the electrolytic apparatus such that the second electrolyte solution contacts the anode and the cathode, the second electrolyte solution comprising chitosan ions; and
- 15 passing a current between the anode and the cathode to promote the growth of a chitosan layer on top of the calcium phosphate containing compound on the cathode.

38. The method as set forth in claim 37 wherein the cathode is comprised of a conductive material selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, tin, cobalt, aluminum, chromium, molybdenum, tungsten, titanium vanadium aluminum alloys, cobalt chromium molybdenum alloys, and

5 combinations thereof.

39. The method as set forth in claim 37 wherein the calcium phosphate containing compound is brushite.

40. The method as set forth in claim 37 further comprising the step of treating the cathode having the calcium phosphate containing compound and chitosan compound

deposited thereon with a base solution to produce a composite coating comprised of chitosan and hydroxyapatite.

41. The method as set forth in claim 37 wherein the cathode is subjected to a base solution after the growth of the calcium phosphate compound but prior to the growth of the chitosan layer to convert the calcium phosphate compound to hydroxyapatite.

42. The method as set forth in claim 37 wherein the current passed between the anode and the cathode during the calcium phosphate compound growth and the chitosan layer growth is from about  $1 \times 10^{-3}$  Amp/cm<sup>2</sup> to about 1 Amp/cm<sup>2</sup>.

43. The method as set forth in claim 37 wherein both the first and second electrolyte solution have a pH of from about 1.5 to about 7.

44. A prosthetic device having electrolytically deposited onto a surface thereof a bio-compatible composite layer, the bio-compatible composite layer comprising hydroxyapatite and chitosan.

45. A prosthetic device as set forth in claim 44 wherein the prosthetic device is comprised of a material selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, tin, cobalt, aluminum, chromium, molybdenum, tungsten, titanium vanadium aluminum alloys, cobalt chromium molybdenum alloys, and combinations thereof.

46. An article as set forth in claim 45 wherein the prosthetic device further comprises a second coating selected from the group consisting of carbon and nitride.

47. A method of preparing a substrate having a composite coating thereon, the method comprising:

introducing a cathode and an anode into an electrolytic apparatus, the cathode comprising a substrate to be coated with the composite coating;

5           introducing an electrolyte solution in the electrolytic apparatus such that the electrolyte solution contacts the cathode and the anode, the electrolyte solution comprising calcium ions and phosphate ions;

          passing a current between the anode and the cathode to promote the growth of brushite on the cathode;

10           removing the brushite coated cathode from the apparatus and coating the cathode with an aqueous solution comprising chitosan; and

          evaporating the water from the aqueous coating to provide a composite coating comprising brushite and chitosan.

48. The method as set forth in claim 47 further comprising converting the brushite to hydroxyapatite after the evaporation of the water.

49. The method as set forth in claim 47 wherein the aqueous solution comprises from about 0.1% (by weight) to about 5% (by weight) chitosan.

50. The method as set forth in claim 47 wherein the aqueous solution further comprises a growth factor.

51. The method as set forth in claim 50 wherein the growth factor is transforming growth factor- $\beta$ 1.

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